

(MAGNETO)THERMOPOWER AND THERMAL CONDUCTIVITY IN OXIDES AND SULFIDES*

According to their low toxicity and robustness against oxidizing conditions, thermoelectric ceramics of transition metal oxides or sulfides have been studied by many research teams over the world. The p-type oxides such as layered cobaltites $\text{Na}_x\text{Co}_2\text{O}_4$ or $[\text{Bi}_{1.7}\text{Co}_{0.3}\text{Ca}_2\text{O}_4]^{\text{RS}}_{0.6}\text{CoO}_2$ [1, 2], perovskite and hollandite ruthenates SrRuO_3 , $\text{ACu}_3\text{Ru}_4\text{O}_{12}$ ($\text{A} = \text{Na}, \text{Ca}, \text{Ca}_{0.5}\text{La}_{0.5}, \text{La}$) and $\text{A}_{1.5}\text{Ru}_{6.1}\text{Cr}_{1.9}\text{O}_{16}$ ($\text{A} = \text{Sr}, \text{Ba}$) [3–5], exhibit a spin driven contribution to the thermopower which can be revealed by magnetothermopower (MTEP) measurements.

We have more recently shown for the first time that MTEP effect also exists in magnetic sulfides such as the CuCrTiS_4 spinel SPS densified ceramic [6]. These results allowed to generalize the effect of magnetism on the Seebeck coefficient (S).

This is in marked contrast with the control of the thermopower by tuning the charge carrier concentration in n-type oxides as $\text{Zn}_{1-x}\text{In}_x\text{O}$ [7] and sulfides as Fe_xTiS_2 [8]. For the latters, the chemical substitution or intercalation are efficient to reduce the lattice part of the thermal conductivity (κ_l) as well as to optimize the power factor (S^2/ρ , where ρ is the electrical resistivity). In that respect, the pyrites family is an interesting system as in this simple cubic structure, κ_l can be drastically reduced by doping such as the Cu effect in NiS_2 [9] (Fig. 1).

Through several examples, including tellurides such as the Sb_2Te_3 /graphite nanocomposites [10], the different routes to improve the thermoelectric properties of thermoelectric dense ceramics will be proposed.

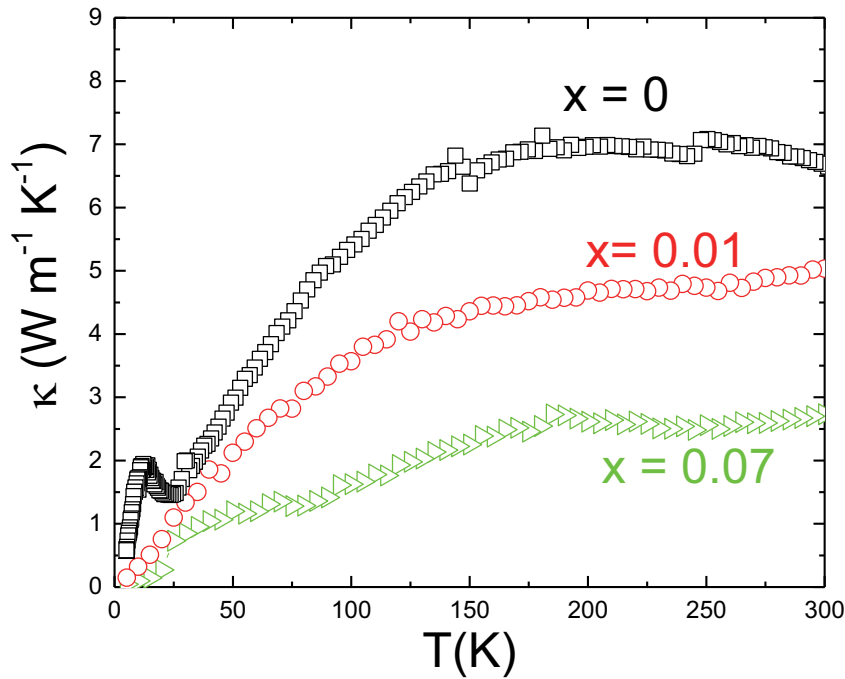


Fig. 1. Thermal conductivity κ of $\text{Ni}_{1-x}\text{Cu}_x\text{S}_2$ ceramics; with 7%-Cu only, κ is decreased by a factor of 2 at RT

References

1. Wang Y., Rogado N. S., Cava R. J., Ong N. P. Spin entropy as the likely source of enhanced thermopower in $\text{Na}_x\text{Co}_2\text{O}_4$ // *Nature*. – 2003. – V. 423. – P. 425–428. <https://doi.org/10.1038/nature01639>
2. Scaling Behavior in Thermoelectric Misfit Cobalt Oxides / P. Limelette et al. // *Phys. Rev. Lett.* – 2006. – V. 97. – No. 0046601. <https://doi.org/10.1103/PhysRevLett.97.046601>
3. Insensitivity of the band structure of substituted SrRuO_3 as probed by Seebeck coefficient measurements / Y. Klein et al. // *Phys. Rev. B*. – 2006. – V. 73. – No. 052412. <https://doi.org/10.1103/PhysRevB.73.052412>
4. Hébert S., Daou R., Maignan A. Thermopower in the quadruple perovskite ruthenates // *Phys. Rev. B*. – 2015. – V. 91. – No. 045106. <https://doi.org/10.1103/PhysRevB.91.045106>
5. Pawula F., Hébert S., Pelloquin D., Maignan A. Two new magnetic hollandites $\text{A}_{1.5}\text{Ru}_{6.1}\text{Cr}_{1.9}\text{O}_{16}$ (A = Sr, Ba): magnetoresistance and thermopower // *J. Mater. Chem. C*. – 2019. – V. 7. – P. 86–94. <https://doi.org/10.1039/C8TC04518F>

6. Berthebaud D., Lebedev O. I., Maignan A., Hebert S. Magnetothermopower and giant magnetoresistance in the spin-glass CuCrTiS_4 thiospinel // J. Appl. Phys. – 2018. – V. 124. – No. 063905. <https://doi.org/10.1063/1.5036828>
7. Phonon scattering and electron doping by 2D structural defects in In/ZnO / J. B. Labégorre et al. // Applied Materials and Interfaces. – 2018. – V. 10. – P. 6415–6423. <https://doi.org/10.1021/acsami.7b19489>
8. Anisotropic thermal transport in magnetic intercalates Fe_xTiS_2 / F. Pawula et al. // Phys. Rev. B. – 2019. – V. 99. – No. 085422. <https://doi.org/10.1103/PhysRevB.99.085422>
9. Thermoelectric properties, metal-insulator transition and magnetism: revisiting the $\text{Ni}_{1-x}\text{Cu}_x\text{S}_2$ system / A. Maignan et al. // Phys. Rev. Materials. – 2019. – V. 3. – No. 115401. <https://doi.org/10.1103/PhysRevMaterials.3.115401>
10. Sb_2Te_3 /graphite nanocomposite: A comprehensive study of thermal conductivity / S. Das et al. // J. Materiomics. In press. <https://doi.org/10.1016/j.jmat.2020.11.014>.

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